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DETERMINATION OF CARBON IN COAL COMBUSTION RESIDUES

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ABSTRACT

A new method has been developed at CANMET for the analysis of carbon in combustion residues. In this method, the sample is first dried and ground to a fine powder, and then digested in a mixture of acids. The insoluble residue is then separated by filtration and its weight determined by difference. The filtrate is kept for the analysis of elements by induction coupled plasma spectrometry. A detailed description of the method is contained in the first part (A) of this report.

The second part (B) gives a description of the tests performed to evaluate the method and clarify the meaning of its results. It is found that the insoluble residue after the acid digestion contains the elementary carbon and most of the organic carbon (i.e., carbon combined in organic matter). However, an appreciable fraction of the organic carbon, which depends on the sample matrix, may be lost in the acid treatment. No losses were observed in samples from boiler residues, but losses of up to about 50% were found for samples from fluidized bed combustion. Analyses of spiked samples and of standards also indicated losses of organic matter. A modification of the acid attack appears thus necessary to improve the method. For a given sample, the results of the method were found reproducible within 4%.

The third part (C) provides a critical review of the existing

methods for determining the different kinds of carbon (total, elementary, inorganic and organic) and a selected bibliography.

RESUME

Une nouvelle méthode a été développee à CANMET pour la détermination du pourcentage de carbone dans les résidus de combustion. Dans cette méthode, les échantillons sont d'abord séchés et pulverisés, et puis soumis à une digestion acide pour solubiliser la partie inorganique, qui est analisée séparément. La proportion de résidu insoluble par rapport à l'échantillon est alors déterminée. Cet exposé contient dans une première partie (A) la description détaillée de la méthode.

Une deuxième partie (B) contient une description des essais réalisés pour évaluer la méthode et pour éclaircir la signification des résultats. On trouve que le résidu insoluble à l'attaque acide contient le carbone élémentaire et une fraction plus ou moins grande du carbone organique (carbone combiné en substances organiques). Les pertes de matière organique pendant l'attaque acide dépendent de la matrice de l'échantillon. On trouva qu'il n'y avait pas de pertes pour des échantillons provenant d'une chaudière, mais qu'elles étaient considérables (atteignant à peu près le 50%) pour des résidus de lits fluidisés. L'analyse de standards et d'échantillons avec carbone organique et élémentaire ajoutés confirme l'attaque de la matière organique pendant la digestion. Donc, une modification de l'attaque acide paraît nécessaire pour améliorer la méthode. La reproductibilité de la méthode est de 4%.

Une troisième partie (C) de l'exposé consiste en un résumé critique des méthodes courantes pour la determination des différentes sortes de carbone (total, élémentaire, inorganique et organique) et une sélection bibliographique des méthodes et études sur ce sujet.

The present work has been performed in fulfillment of the contract with CANMET - Energy Research Laboratories, DSS File No. 63SS.23440-8-9172, with the aim of evaluating a new analytical method developed in the CANMET Laboratories. This final report consists of a set of 3 partial reports, as follows.

A - The CANMET method

This is a complete description of the new method.

B - Critical evaluation of an indirect method of measuring carbon in solid combustion residues

This report summarizes the work performed in order to assess the validity of the new CANMET method.

C - Review of bibliography on the determination of carbon

This is a review of the analytical methods existing for the determination of elemental, inorganic, organic and total carbon. It contains brief descriptions and comments on the methods, and a list of references.

A

The CANMET Method

CONTENTS

I - Introduction

II - Experimental

1) Apparatus and materials used

2) Reagents

III - Procedure

I - Introduction

The CANMET method is a new method for determining carbon in combustion residues, both from conventional pulverized coal combustion and from circulating and bubbling fluidized bed combustion (FBC). The sample is first dried and ground to a fine powder. A weighed amount is digested in a mixture of acids, using a special microwave digestor. The insoluble residue is then separated by filtration and weighed by difference. This residue is composed of elemental carbon (graphite or amorphous) and organic matter, as will be discussed in Section IX (for the definitions of the different types of carbon, see Part C, Introduction).

The filtrate is used for the analysis of elements using an Induction Coupled Plasma Spectrometer.

In this work 12 samples were analyzed simultaneously; the duration of these analyses was a working day.

II - Experimental

1) Apparatus and materials used.

- Analytical balance (to 0.1 mg) Mettler HL 32.

- Microweighing glass funnels (55 mm x 25 mm).

- Microwave Digestion System MDS-8ID (CEM Corporation, U.S.A.). Maximum power: 650 W.The system includes 12 teflon sample vessels (120 ml capacity), capable of resisting a pressure up to 6.5 atm and 200 degrees C. The vessels are distributed over a turntable and are connected with a collection vessel in the middle of the turntable by teflon tubes. Each vessel is provided with a relief valve. This valve is a disc which is seated between the vessel and the cap (See figures 1, 3, 4 and 5).

- A capping station (CEM) provided with a reversible electric motor; the capper serves to tighten the cap to a fixed torque and to loosen it after cooling (see Fig. 2).

- Cooling tank, with water supply at room temperature.

- Dessicating chamber (room temperature).

- Millipore filters: cellulose, 47 mm diameter and 0.65 micrometer pores.

- Vacuum pump for filtration.

- Petri dishes, 9 cm diameter.

- Complete polyethylene filtering system.

- Twelve (12) 250 ml polypropylene volumetric flasks.

2) Reagents - All chemicals of ultrapure quality.

- Hydrofluoric acid, 48.4 %.

- Hydrochloric acid, 12 M.

- Nitric acid, 17 M.

- Aqua regia (stock): (750 ml HCl + 250 ml HNO3) diluted to 2 liters.

- Distilled water (Barnstead unit).

III - Procedure

1 - All glass and plastic ware is cleaned following the ASTM norms.

2 - The gross sample is crushed, blended, quartered and then pulverized to produce approximately 10 g of a less than 200 mesh (75 micrometer) net sample.

3 - About 100 mg of net sample are exactly weighed into a pre-weighed micro-weighing funnel. The weight is determined by difference. Much care is used to avoid losses of dried powder in the operation.

4 - The sample is dried overnight in a dessicator, and weighed to determine any moisture loss.

5 - The sample is transferred quantitatively to the teflon vessel with the aid of 5-10 ml water.

The 12 samples used in one operation are worked in the same manner, successively.

6 - 30 ml of aqua regia are added to each vessel, followed by 5 ml of concentrated hydrofluoric acid.

7 - Each vessel, complete with relief valve, is tightened with the help of the capping station, applying an equal torque in each case.

8 - All vessels are placed onto the turntable and connected through the teflon tubes to the central collection vessel.

9 - The loaded turntable is placed in the middle of the microwave stove, which is programmed to work for 2 hours at 96% power. During this process, the turntable is turning, so as to give to each

vessel a similar exposure to the radiation.

10 - After the digestion, the turntable with the vessel is transferred into the cooling tank, which contains water at room temperature. The cooling takes about 1/2 hour. This cooling step is important, because the pressure inside the vessels is relieved, vapours condense (loss of silicon fluoride is thus avoided) and removal of the vessels' cap is facilitated.

11 - The caps of the vessels are removed with the aid of the capping station.

12 - The solution of each vessel is transferred quantitatively to the pump filtering unit, where the filtration takes place by applying a suction of about 25 p.s.i.. The filtration is done through Millipore cellulose filters. These filters were previously kept in dessicator for 24 hours at room temperature, until acquiring constant weight.

13 - Each filtrate is transferred to a 250 ml polypropylene volumetric flask, washing the digestion vessel 3 times with 25 ml portions of water. The volume of the solution is brought to 250 ml with distilled water. It will later be used for determination of elements with the ICP instrument.

14 - The filter and residue is placed and kept overnight on a Petri

dish in the dessicator. In what follows, this residue is called "the acid insoluble" (AI).

15 - The filter with the residue is weighed and replaced in the dessicator until constant weight is obtained. The result is expressed as percent of AI by weight.

16 - Loss on ignition. In order to have a comparison of the final results, an indication of the combustion efficiency (in terms of percentage of carbon burned), and also of the digestion efficiency, the loss on ignition is also determined on a separate aliquot for each sample.

The humidity is first eliminated by drying in a dessicator overnight. The ashing is then performed in a muffle furnace by ramp heating to 500 degrees for 1 hour, followed by ramp heating to 750 degrees C for 2 hours. Vitreosil crucibles are used. The carbonates, organic matter, crystallization water and graphitic carbon are expected to be eliminated in these conditions.

Procedure 16 is normally carried out prior to step 3.

The results obtained for the insoluble residue after the acid treatment in the wet chemistry procedure must be less than (or equal to) the loss on ignition.

B

Critical Evaluation of an Indirect Method of Measuring Carbon in Solid Combustion Residues

CONTENTS

I - Introduction

II - Samples and sets of analysis

III - Analytical methods

1 - Total carbon by combustion and coulometry

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3 - Inorganic carbon

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5 - Elemental carbon

IV - Reproducibility of the CANMET method

V - Direct analysis of samples

VI - Analysis of spiked samples

VII - Analysis and tests with standards

VIII - X-Ray diffraction

IX - Discussion

X - Conclusions and suggestions for improvement and further work

I - Introduction

The experimental study described in this part (Report B) refers to the new method developed in the CANMET Energy Research Laboratory of the Department of Energy, Mines and Resources for the determination of carbon in combustion residues. The method, consisting essentially of determining the insoluble residue remaining after an acid digestion (subsequently referred to as the "acid insoluble", or AI) has been described separately in the Report A.

The object of the study is to assess the validity of such method, and how exactly its results should be interpreted; i.e., whether the acid insoluble determined represents adequately the content in elemental carbon, or the sum of elemental and organic carbon (non-inorganic carbon). An important aspect of this report is to suggest any possible modifications of the method which might be expected to improve the results that can be obtained from it and to clarify their significance. It should be kept in mind that the final aim of these analyses is to estimate the efficiency of the combustion processes.

The carbon contained in a material can be present in different forms: as elemental carbon (C_{el}), either graphitic or amorphous, as inorganic carbon (C_{in}), which is normally in the form of carbonate, and as a component of organic compounds (C_{org}). These definitions and the analytical problems involved in differentiating the different kinds of carbon in a material have been summarized in the separate Report C.

II - Samples and sets of analyses

A set of 13 samples was chosen: 8 from a Pilot-Scale Research Boiler (PSRB), which is a conventional pulverized coal fired boiler (Fig.6); and 5 taken from three fluidized bed units, the pilot scale bubbling FBC at Queen's University (Fig 8), the pilot-scale circulating FBC at the University of British Columbia (Fig.7) and the 22 MW_e circulating FBC boiler at Chatham, New Brunswick. These samples provide different matrices in which the carbon determinations were performed. The list of samples is given in Table 1. The sample numbers or designations are given in the first column. The sampling site is indicated in the second column, where the numbers refer to indications in the Fig. 6, representing schematically the combustion plant from CANMET. The origin of the samples are given in the third column.

Four sets of analyses were performed:

- 12 determinations of the acid insoluble were made on single

sample, in order to evaluate the reproducibility of the CANMET method. These analyses were performed in the CANMET laboratory. Section IV discusses the reproducibility of the method.

- Analysis of the 13 selected samples. See Section V.
- In addition to the above 13 samples, a selection of 3 samples was used to spike them with elemental carbon (graphite) and organic carbon (anthracene) and perform analysis of the spiked samples. See Section VI.
- 3 standard samples were prepared, and analysis performed on them. See Section VII.

The analyses consisted of the determination of total carbon (by two methods), inorganic carbon and organic carbon, while the "acid insoluble" (cf. Part A, Procedure, Section 14) was determined in the CANMET laboratory on the same samples, by the new method. The elemental carbon was derived by difference, subtracting inorganic and organic carbon from total carbon.

III - Analytical methods

The description of the CANMET method is given separately. Here the methods for the other determinations are described.

1 - Total carbon by combustion and coulometry (C_{tot})

The combustion and coulometric determinations were performed in the Model 5011 Carbon Dioxide Coulometer, from Coulometrics, Inc. (Standard Method ASTM D-4129-82).

A sample of 20 to 100 mg is weighed, using a microanalytical balance, in a small Pt boat and inserted in the combustion tube. The combustion is performed at 950°C in a current of oxygen previously purified by passage through a scrubber with a potassium hydroxide solution, to eliminate any carbon dioxide, and magnesium perchlorate as desiccant. The combustion gas passes through a scrubber with acid dichromate on silocel and manganese dioxide, that oxidize and remove NO_x products. Other non-carbon combustion products, such as SO_2, SO_3, HX (hydrogen halides), are removed from the gas stream by other chemical scrubbers.

The gas from the combustion tube goes into a coulometric cell filled with a partially aqueous medium containing ethanolamine and a colorimetric indicator. The CO_2 reacts with the ethanolamine to form a strong titratable acid which causes the indicator colour to fade. The titration current automatically turns on and electrically generates base (silver electrode) to return the solution to its original colour. A summary of the chemical reactions occurring in the coulometer cell is given below.

$$CO_2 + HOCH_2CH_2NH_2 = HOCH_2CH_2NHCOOH$$

(where the organic compound at the left is ethanolamine, and the one at the right is hydroxyethylcarbamic acid)

$$Ag^{\circ} = Ag^{+} + e^{-}$$

$$2\ H_2O + 2\ e^{-} = H_2 + 2\ OH^{-}$$

$$HOCH_2CH_2NHCOOH + OH^{-} = HOCH_2CH_2NHCOO^{-} + H_2O$$

The detection limit of the method is 0.01% (in g of C/g of sample).

2 - Total carbon by combustion and infrared (C_{tot})

The total carbon was also determined by use of the LECO instrument, in which the carbon is oxidized by combustion at 1100°C in a pure O_2 atmosphere. The CO_2 is measured by infrared absorption. As in the previous method, non-carbon combustion products are previously removed by chemical scrubbers. The detection limit is 0.01%. (Standard Method ASTM E-1019-27a).

3 - Inorganic carbon (C_{in})

Carbon dioxide from carbonates was evolved from the sample by treatment with 2 N $HClO_4$, and then determined coulometrically (cf. ASTM D 513-82). The detection limit is 0.01%.

4 - Organic carbon (C_{org})

The organic carbon was determined by heating at 500°C and measuring the CO_2 by coulometry. This was done in the same instrument used for the total carbon (section III-1 above). The detection limit is 0.05%.

5 - Elemental carbon (C_{el})

The elemental carbon was determined by difference:

$$C_{el} = C_{tot} - C_{in} - C_{org}$$

In applying this formula, the coulometric determination for the total carbon was used (rather than the thermal-infrared), as being more consistent with the result for organic carbon, also obtained coulometrically.

IV - Reproducibility of the CANMET method

In order to assess the reproducibility of the CANMET method, a sample was chosen (the sample was designated as A-126486, and was a residue obtained from the combustion of coal with the PSRB) to determine 12 times the content in AI% (acid insoluble). The results were (analyses performed in CANMET Laboratories):

10.90; 11.29; 11.33; 11.30; 11.91; 12.20

11.95; 12.04; 11.88; 12.10; 12.38; 12.20

This gives an average of 11.79, with a standard deviation of 0.47 (or 4.0% of the average).

V - Direct analysis of samples

The results of the analysis of the 13 selected samples

are given in Table 2. The following remarks can be made.

Both methods for the determination of C_{tot} give consistent results.

In the samples from the Pilot-Scale Research Boiler (first 8 samples), the content of elemental carbon in the acid insoluble is either comparable with that of organic carbon (samples A-126686 and A-126786) or much smaller. In the FBC samples, the elemental carbon content is either 0 or very little, with the exception of S10-609#2D, for which it is appreciable, but still much smaller than the content of organic carbon.

The AI results give values consistently close to or slightly higher than total carbon for the PSRB samples. Practically no organic carbon has been attacked in these samples. In the FBC samples (remaining 5 samples), AI gives consistently lower results than total carbon, but much higher than elemental carbon (which in these samples is in low content or absent), indicating that part (but only a part) of the organic carbon has been eliminated by the treatment.

The values of the loss on ignition (LOI) are, as expected, approximately equal or larger than AI.

VI - Analysis of spiked samples

Three samples were selected; two from PSRB and one from

FBC. The 3 selected samples, whose composition was known (Table 2), were spiked by the addition of known amounts of elemental carbon, in the form of pure graphite, and of organic carbon, in the form of anthracene of known purity. Thus the spiked samples contain the contribution of carbon from the original sample (diluted by the additions) plus the added amounts. Subtracting from the analysis of the spiked sample the composition of the original sample (corrected for the dilution) should give the known amounts of added C_{el} and C_{org}, if the two analyses (original and spiked sample) are correct. The results obtained are summarized in Table 3. For each spiked sample, the table contains four lines:

First line - Sample number followed by "S": analysis of spiked sample.

Second line - Sample number followed by "C": analysis of original sample corrected for the dilution effected by the spiking; i.e., contribution to the spiked sample of the original contents of C_{tot}, C_{in}, C_{org}.

Third line - D found: difference of first line minus second line, indicating added amounts, according to analysis.

Fourth line - D real: real amounts added.

The table shows that the AI data give 80 to 82% of the total carbon in the three samples. Presumably, the carbon is not totally recovered because an appreciable amount of the organic carbon has been eliminated. This is supported by the results of the first two samples, whose analyses show 29% and 46% less organic

carbon than the added amount. The analysis of the third sample shows an excess of organic carbon of 19%, which must be attributed to experimental error.

VII - Analysis and tests with standards

The standards were prepared with $CaSO_4$ as matrix, pure graphite as elemental carbon, $CaCO_3$ as inorganic carbon (factor to calculate as C: 0.1199), and anthracene as organic carbon (purity 93.8%, based on C determination in triplicate; factor to calculate anthracene as C: 0.9435).

The results of the analyses are summarized in Table 4. AI was determined in duplicate, and the average is indicated in the table.

The table shows that AI agrees reasonably well with the total carbon, when this is pure graphite (standard 1). For standard 2, AI is less than total carbon; about 29% of the organic carbon seems to have been eliminated by the treatment. For standard 3, AI also gives a result lower than elemental + organic carbon (inorganic carbon is not supposed to be included in AI), presumably because about 10% of the organic carbon has been eliminated.

Some tests were performed using standard sample 1 (containing graphite) and standard 2 (containing anthracene), with two different acid solutions. The samples were digested for 2.5 hours on a hot plate, below the boiling point (70-80°C). After

cooling and diluting, filtration was operated under vacuum through the same Millipore filters used in the CANMET method. The filters were weighed following drying at about 50°C for 2 hours, before and after use. The total carbon was determined before and after the attack with acids, and the results calculated. The following tests were performed with each sample:

1) With HCl 1:1. The recovery of carbon was between 95 and 100% for standard 1 (graphite) and about 75% for standard 2 (anthracene).

2) With aqua regia (3 volumes of HNO_3 + 1 volume of HCl), diluted 1:1. The recovery of total carbon was about 82% for standard 1 and about 75% for standard 2.

Thus, with this type of treatment, in which the digestion is performed at higher temperature than in the CANMET method, it appears that the organic matter is appreciably attacked even without the presence of HNO_3, but graphite is not attacked unless the oxidizing HNO_3 is present.

VIII - X-Ray diffraction

In order to check whether any crystalline compounds remained in the acid insoluble after the CANMET treatment (for instance, any silica not completely eliminated by the HF), an X-ray diffraction test was made of the filter with the acid insoluble deposit from sample A-126486 remaining after filtration. Separate

tests were made with clean filter.

The diffractogram of filter with acid insoluble showed the presence of major silver, trace willemseite (nickel-rich talc) and amorphous carbon. The silver is contained in the filter itself, because the diffractogram of the clean filter also revealed its presence. It may be concluded from these tests that no crystalline material remains as part of the "acid insoluble".

IX - Discussion

Determining the total content of the elemental carbon plus the organic carbon remaining in combustion residues is an appropriate way of evaluating the efficiency of the combustion process. However, a distinction between organic and elemental carbon, giving their separate contributions, might also be desirable. This distinction is a much more difficult analytical problem than the determination of the sum of both elemental and organic carbon.

The CANMET method is part of a suite of analyses determining the major elements in the residue, as well as the acid insoluble fraction. Thus, the method has two goals; first, to digest the entire mineral content and second, leave the carbonaceous combustible content for analysis. The procedure is

delicate, but it is clear that it gives reproducible results, as it has been shown in the test described in Section IV. It remains to consider the exact meaning of the "acid insoluble" measurement obtained by this procedure.

The examination of the results obtained in this study show clearly, in the three sets of analyses of Sections V-VII, that the "acid insoluble" obtained by the CANMET method corresponds roughly to the sum of elemental and organic carbon, but that a certain amount of the organic matter is eliminated by the treatment. This loss appears strongly dependent on the matrix in which the organic matter is contained. Thus, perusal of Table 2 indicates that there is practically no loss in the first 8 samples from PSRB, consisting of the residues of coal combustion without additives. In the 5 other samples, consisting of residues from fluidized bed combustion, the losses of organic carbon are very variable, reaching as much as 44% in sample Q-860114 and 48% in BC-Run 14. The analyses of Table 3 performed on spiked samples of different matrices, showed losses of 33 to 38%, as mentioned in Section VI. In the case of the standards, which had a matrix of $CaSO_4$, the loss of anthracene was found of about 29% in standard 2 and only 5% in standard 3.

These losses of organic material are surely enhanced by the use of HNO_3 in the acid digestion (if not entirely due to it), since it is known that oxidant mixtures attack the organic compounds and even the graphite, if the treatment is sufficiently strong. It is doubtful, with the present information, whether the

organic matter would also be attacked if the HNO_3 was not present, since the CANMET digestion method uses only low temperatures.

X - Conclusions and suggestions for improvement or further work

As it stands, the CANMET method gives an approximate value of the sum of elemental and organic carbon in the samples, but an appreciable fraction of the organic matter, which depends on the matrix, may be eliminated in the treatment. The obvious suggestion for improvement is to experiment with a non-oxidant acid treatment, i.e,, omitting the use of HNO_3; perhaps also varying the acid concentrations. The tests should be done with standards, or with samples of well known composition.

Further experimentation could be done to adapt the method to the separate determination of elemental and organic carbon. For this purpose, solutions of much stronger oxidant strength should be tried. The treatment should be strong enough to eliminate all the organic matter, but not sufficiently strong to attack any of the elemental carbon. A variety of mixtures could be tried with this purpose; for instance, perchloric acid, hydrogen peroxide, alkali and ethanol, etc. In each case, varying the conditions of concentration or temperature to reach the appropriate efficiency

to effect the separation of organic and elemental carbon. Such tests would have to be performed with different types of matrices.

C

Review of Bibliography on the Determination of Carbon

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5 - Determination of elemental and organic carbon

References

a) Recommended bibliography

b) References by alphabetic order

1 - Introduction

Carbon is present in a large variety of natural and industrial products. It may be the predominant element, as in coal, or else a minor or trace component, as in steel.

It is customary to classify the carbon present in a sample into three main categories:

1) Elemental carbon (C_{el}). This is sometimes taken as synonymous with black carbon or graphitic carbon, although graphite has a well defined crystal structure and elemental carbon can also be in an amorphous state. The symbol C_{el} will be used to indicate the concentration of C in a material.

2) Inorganic carbon (C_{in}). This is practically synonymous with carbonate carbon, since carbonates are the only common type of compounds in which non-organic combined carbon appears. C_{in} should be understood as the concentration of the carbon (expressed as C) which is in the form of $CO_3^=$.

3) Organic carbon (C_{org}). This is the concentration of carbon combined in any kind of organic compound. While for the study of some materials, it may be desirable to classify the organic compounds in different groups or identify the organic compounds present, we shall not consider this type of distinction in this bibliographic summary (see, for that respect, Karr, 1978, Vol.II).

4) Total carbon (C_{tot}) is defined by the total concentration of

carbon element. Thus:

$$C_{tot} = C_{el} + C_{in} + C_{org} \qquad (1)$$

Analysis of carbon may be of interest in many types of materials. We shall mention some of those that have received special attention:

- coal and coke
- graphite (industrial or natural)
- oil shales
- fly ash
- steel, iron, other metals
- soil
- marine or fluvial sediments
- atmospheric aerosol

Our particular interest lies in the analysis of carbon in wastes of coal combustion or fluidized bed combustion, where limestone is being used in order to fix the S contained in coal in the form of sulfate. As in many other materials, the determination of C_{in} does not present an analytical problem. Carbonates can be easily determined by displacement of CO_2 with acids and dosage of the carbon dioxide by any of a number of techniques. Sometimes the quantitative determination of carbonates is not even required, so that their elimination is merely a previous step to the determination of the elemental and organic carbon.

Obviously, if a complete description is desired in terms of

the 3 types of carbon, only 3 of the 4 quantities appearing in equation (1) need to be determined; the fourth one is obtained by difference. The total and inorganic carbons are the two most easily determined quantities. The main analytical problem consists in differentiating between the elemental and the organic carbon.

Regarding the bibliographical search, no information was found referring specifically to wastes of coal combustion, either with or without the addition of limestone. The appropriate methods are to be found mainly in analytical work with soils (whose composition is extremely variable and may be more or less similar to the materials of present interest) and in work with aerosols. Matrices such as coal, with an overwhelming content of carbon, or steel, with only trace amounts of carbon and an overwhelming content of iron that must be dissolved, are quite dissimilar to the matrices of our interest.

2 - Determination of total carbon

The determination of C_{tot} is based in the total conversion of the carbon element into carbon dioxide, which can then be determined by various methods (see Section 4). The oxidation procedures are usually grouped into two categories:

- Dry ashing, which usually implies ignition of the C-containing material in air or in a stream of oxygen.
- Wet ashing, which makes use of liquid oxidizing agents, such as sulfuric or perchloric acids.

Oxidations can also be carried out in fused-salt media; in this case the most common flux utilized is sodium peroxide.

a) Preparation of the sample

While some organic substances may not need any special preparation for the combustion, other samples are ground to a specified degree of fineness. For coal and coke, the ASTM norm D 3178-84 specifies that the sample shall be pulverized to pass No. 60 (250 micrometers) sieve and well mixed according to given methods. Soils are treated similarly. ASTM norm for steel, iron, nickel and cobalt alloys stipulates that the sample should be uniform in size, but not finer than 40 mesh.

b) Dry combustion methods

A variety of suitable apparatus have been used to determine both C and H in organic or coal samples by combustion and absorption of the CO_2 and H_2O produced. The weighed sample is placed in a glazed porcelain, fused silica or Pt boat, inside a high silica glass or fused quartz combustion tube. Purified oxygen circulates through the tube, and the combustion products are carried by the gas stream into an absorption train. In order to ensure complete oxidation of combustion products and complete removal of interfering substances such as oxides of sulfur and halogens, the combustion tube is packed with CuO and $PbCrO_4$ or Ag. PbO_2 may also be used, as well as a Pt gauze acting as a catalyst. In precise work the oxides of nitrogen are removed prior to

absorption of CO_2 by inserting an absorption tube containing MnO_2. The combustion tube is usually heated by a furnace to a temperature of 850-900 degrees C. Such a procedure is described in full detail in the norm ASTM D 3178-84 for analysis of C and H in coal and coke.

Among the numerous alternative procedures that have been proposed, all based on the same principles, but differing in the apparatus, the oxidizing agents and the purification train, the following should be mentioned: Jackson (1958), who recommends use of an induction furnace, Young and Lindbeck (1964), Stewart et al. (1964). (Cf. Hesse, 1971, Chapter 11).

The method and equipment used by the ASTM and ISO 625 norms is similar in many respects (tube length, temperatures in the different furnace sections). In the method ISO 609, the sample is burned in a rapid current of O_2 at a high temperature (1350°C) in an impervious tube (See Karr, 1978).

Automatic elemental analyzers are frequently used for simultaneous determination of carbon, hydrogen and nitrogen (CHN analyzers). They are based on two general procedures. One involves the separation of CO_2, N_2 and H_2O by a gas-liquid chromatographic column. The other involves separation by means of specific absorbents for water and for carbon dioxide, with the resulting change in composition of the gas mixture being measured. Thermal conductivity is the detection method in both techniques. Carbon is oxidized in a furnace to CO_2 and CO, and the oxidation to CO_2 is

completed by CuO. (See Willard et al., 1974).

The LECO furnace is a commercial instrument used for the simultaneous determination of carbon and sulfur by combustion, followed by the infrared determination of the products.

Arthur et al.(1987) have compared the performance of different commercial analyzers. They found that the LECO, the Rock-Eval II and two different CHN analyzers, gave comparable results for organic carbon, with the exception of the two CHN analyzers when they were used for acid treated samples. The carbonate bomb (see below) and the determination of calcium carbonate from total Ca by X-ray fluorescence and inductively-coupled plasma gave consistent results for inorganic carbon, while CHN analyzer overestimated the carbonate.

The combustion can also be performed in sealed containers. This can be done in commercial "bombs" (carbonate bomb technique; see, for instance, Arthur et al., 1987) or simply in a closed flask, in an atmosphere of O_2 (see, for a summary of these techniques, MacDonald, 1965). The reaction products are absorbed in a suitable solvent before the reaction vessel is opened, and the solution is subsequently analyzed.

Cahill et al. (1984) have described the application to aerosols of a number of modern techniques to perform the complete elemental analysis (including that of carbon).

c) Wet ashing

Solutions of strong oxidizing agents will decompose organic matter. This is the basis of the wet ashing. However, the usual procedure is to either predetermine carbonates or just eliminating them by decomposition (if they are not to be quantitatively determined). The wet ashing itself is then used for the remaining carbon (elemental and organic), and therefore the discussion is left to Section 5.

d) Peroxide fusion

Sodium peroxide is a strong oxidizing agent. When used as a flux with the sample, organic matter reacts rapidly with it in the melt, all carbon being converted into carbonate. As the reaction may be violent, the peroxide fusion is carried out in a sealed heavy-walled steel bomb. Oxidation is initiated by passing a current through a heating wire, and continues by itself to completion. Appropriate bombs are available commercially (e.g., Parr Instrument Co., Moline, Illinois). One of the main disadvantages of this method is the large ratio of flux to sample (e.g. 200) necessary; this leaves a water soluble material with a great excess of alkali.

3 - Determination of inorganic carbon

The decomposition of carbonates is readily accomplished by treating the sample with acid (e.g. HCl 1:1) and heating. The CO_2 evolved can be collected and analyzed (see Section 4), or else its

content may be derived from the loss of weight of the sum (acid solution + sample); in the latter case, contact between the acid and the sample must be prevented until the initial weight is determined, and losses of other gases than CO_2 (in particular, water vapour) must be prevented.

A summary of such methods can be found in N. H. Furman, 1966.

The inorganic carbon can also be differentiated from the organic carbon by the so-called "difference-on-ignition" method. The total carbon is first measured in untreated dry samples by standard CHN-analysis (using the modern automatic analyzers). Then the organic carbon is removed by combustion at 500°C in a muffle furnace for 16 hours, and the residual carbon is measured on the CHN-analyzer. The difference gives the organic carbon. In this method, any elemental carbon is included with the total carbon, but is not differentiated. Kristensen and Andersen (1987) have compared the performance of the acidification method and the difference-on-ignition method when applied to marine sediments, using a CHN-analyzer. (See also Dean, 1974).

4 - Determination of carbon dioxide

Most of the determinations of carbon, in any of its forms, are based on separating it from the sample in the form of CO_2. The analysis must be completed in each case by determining the CO_2 obtained in the procedure. This can be done by a variety of methods, which will now be briefly described.

a) Gas volumetry

Sulfur compounds, if present, are removed by MnO_2, the CO_2 and excess oxygen are collected and measured in a burette, then passed through an absorption vessel containing potassium hydroxide; the difference in volume before and after absorption in potassium hydroxide is the CO_2 evolved.

b) Gravimetry

The gas carrying the CO_2 (usually air or O_2) passes first through a water absorber (e.g. ASTM D 3178 uses anhydrous magnesium perchlorate of approximately 2.38 to 0.35 mm size; concentrated sulfuric acid or other desiccants can also be used). The dried gas passes then through a weighed tube or container, in which is the CO_2 absorber, usually "ascarite" (sodium hydroxide on asbestos); other CO_2-absorbing materials can also be used, like soda-lime or a strongly alkaline solution. The weighed absorbing trap must also have a desiccant following the CO_2-absorbent, in order to avoid losses of water vapour. The amount of CO_2 absorbed is determined by weight difference.

c) Acidimetry

The CO_2 can be absorbed in a known amount of standard alkaline solution, and the resulting solution containing the Na_2CO_3 and the excess of NaOH is analyzed by titration with acid, following well known procedures (see for instance, Skoog and West, 1976, Chapter 11).

d) Titrimetry

Another titrimetric method (Jones et al., 1965) is to absorb the CO_2 in dimethylformamide containing a small amount of monoethanolamine and titrate with a standard solution of tetra-n-butylammonium hydroxide in a benzene-methanol-toluene mixture, with thymolphthalein as indicator. Other modified titration systems may be seen in Metters et al., 1972.

e) Manometry

The carbon dioxide is collected in a cold trap immersed in liquid nitrogen, the carrier gas is pumped out of the system and the CO_2 is vaporized into a calibrated volume and its pressure is measured. (Harrison, 1979; Cook and Speight, 1956; Dunnill and Kent, 1970).

f) Infrared

Various instruments (LECO, Hilger "Autocarb" and "Dynacarb") utilize the absorption of infrared radiation by the combustion products, comparing it with that of pure carrier gas. (Harrison, 1979; Bagshawe and Scholes, 1974).

g) Gas chromatography

The gas containing the CO_2 can be analyzed by gas chromatography, using a flame ionization detector. The temperature may be programmed through any desired range from ambient to 530°C, or maintained at any selected isothermal value. Carbon evolution rates as low as 10^{-9} g/min can be detected by this method (see Willard et al., 1974).

h) Thermal conductivity

This method, as mentioned above (2b), is used in the automatic CHN analyzers.

i) Conductimetry

The carbon dioxide is collected in sodium or barium hydroxide solution, and the change in conductivity is measured.

j) Coulometry

The CO_2 is collected in alkaline barium perchlorate solution and measured coulometrically (Hobson and Leigh, 1974).

In another procedure, the CO_2 reacts with ethanolamine to form an acid, which is titrated coulometrically (the current generates a base that neutralizes the acid. See ASTM 4129-82; Huffman, 1977).

5 - Determination of elemental and organic carbon

The sum (C_{el} + C_{org}) can be obtained simply by difference, if the total carbon and the inorganic carbon are known. Alternatively, the inorganic carbon can be eliminated by acid treatment and the determination of total carbon in the residue will give the sum of elemental and organic carbon.

The problem becomes more difficult when elemental carbon and organic carbon must be differentiated. This problem has been studied carefully by Cadle et al. (1983) in reference to the atmospheric aerosol.

The separation of organic and elemental carbon has been done by several methods, including thermal, digestion, extraction and optical techniques. The first two are the most important and will

be considered here.

a) Thermal methods

There is no method which will cleanly separate the organic from the elemental carbon. Various analytical methods provide different operating definitions of organic and elemental carbon. One widely accepted definition is that elemental carbon is any carbon which is black and organic carbon is the remainder (excluding carbonates). Thermal stripping of the organic carbon has been used, since it provides one of the fastest means of separating the organic and elemental carbon and can be coupled with very sensitive detectors. Unfortunately, it has been shown that some of the organic carbon can carbonize during this kind of separation process (Huntzicker et al., 1981; Cadle and Groblicki, 1981).

It is generally accepted that, within the limitations mentioned above, the organic matter may be eliminated by heating in air at temperatures between 400 and 500°C, so that the remainder is the elemental carbon. For the analysis of aerosols, Cadle et al. (1983) advocate the following procedure: the sample is heated at 350°C in air and then pyrolyzed in He at a higher temperature that can go from 650 to 950°C to remove the organic carbon; the remaining elemental carbon is determined by combustion in air. The organic carbon is obtained by difference. For samples of unknown nature, the authors recommend 950°C for the pyrolysis in He. They also found that very little elemental carbon is removed by

oxidation at 450°C.

Johnson et al. (1981) separate elemental and organic carbon in aerosols by volatilizing first the organic carbon, which is oxidized to CO_2, then reduced to CH_4 and measured by chromatography with flame ionization detector; the residue contains the elemental carbon, which is oxidized to CO_2 and measured.

Van Iperen and Helder (1985) studied the determination of organic carbon in calcareous marine sediments. They recommend using a CHN-analyzer (microcombustion at 1100°C) after acidification of the sample with 1 N HCl for removal of the inorganic carbon.

b) Digestion methods (wet ashing)

Solutions of strong oxidizing agents will decompose organic matter. The agents commonly used are mixtures of sulfuric and nitric acids, or as a more effective reagent, of perchloric and nitric acid. The hot anhydrous perchloric acid may react explosively with organic material, which means that such a procedure must be used with all the appropriate safety measures.

When elemental and organic carbon must be differentiated, it should be made certain that the digestion method does not attack the elemental carbon. It is known that graphite is not attacked by HCl, H_2SO_4, HNO_3 and HF, though some varieties change their form with HNO_3. On the other hand, graphite is oxidized in chromic acid or in $K_2Cr_2O_7 + H_2SO_4$. (See, for instance, Gmelin, 1968; also King, 1922).

In their study on aerosols, Cadle et al. (1983) tested the

results of several digestion methods: a 0.75h digestion in U.V.-irradiated H_2O_2, a 18h ethanolic-KOH digestion, and a 18h digestion with room-temperature, silver-catalyzed acidic persulfate solution. All these solutions are known as effective oxidizers of organic compounds. The results showed appreciable discrepancies and, in particular, the last of the three methods proved to be too strong, oxidizing most of the elemental carbon. This illustrates the need of a careful choice in the oxidizing agent used to remove the organic carbon without attacking the elemental carbon as well; this choice will also depend on the nature of the analyzed samples.

Rao (1986) collected aerosols in glass fiber filters. These were treated with HF, NH_4OH, HNO_3+HCl, and the residue dried at 150°C to eliminate the organic carbon. Heating at 700°C for 2 hours would eliminate the residual elemental carbon.

Sippola (1983) made a comparison between a dry combustion method and a rapid wet combustion method for determining soil organic carbon. He found that the dry combustion gave results 6 to 7% higher for clay and coarse mineral soils, and 12% higher for organic soils. He attributes to incomplete oxidation the lower results of wet combustion.

Scharf (1966), in analysis of soil, also found that dry ashing methods consistently yielded higher results than a wet ashing method.

Winazakiewicz and Zajaczkowska (1961) used nitration to eliminate lignin and hydrolysis to eliminate cellulose from paper, so as to separate a residue consisting of black carbon and

asbestos.

Albert (1961) also considered the determination of graphite in the presence of non-graphitic carbon. He found that graphite powder gives a solid blue interlamellar sorption compound with cold concentrated H_2SO_4 when in presence of an oxidizing agent.

Regarding the separation of elemental and organic carbon, it can be said in summary that the thermal methods are reliable, within the limitation of possible minor errors (notably carbonization of organic matter). On the other hand, use of digestion methods (wet ashing) must be used with caution, checking that the oxidant mixture and type of treatment used does eliminate the organic matter without attacking the elemental carbon.

References

a) Recommended bibliography

The following references may be particularly useful to initiate the study of bibliography on various specific subjects.

- For soil analysis, see Hesse, 1971.
- For coal and coke, see ASTM - D 3178, ISO 625, ISO 609.
- For steel and metals and for determination of CO_2, inorganic, and total carbon, see Furman, 1966; Harrison, 1979; ASTM E 1019.
- For atmospheric aerosol and in particular for the determination

of elemental and organic carbon, see Cadle et al., 1983.

- For marine sediments, see Kristensen and Andersen, 1987, and references therein.

b) References by alphabetical order

In many of the references, a bold letter between brackets at the end of the reference indicates whether it refers to a particular application or is of a general applicability. The meaning of the letters is as follows. **A**: atmospheric aerosol; **C**: coal, coke, graphite; **D**: sediments; **G**: general; **M**: metals, steel; **S**: soil.

ASTM stands for American Society for Testing and Materials; ISO stands for International Standardization Organization.

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Table 1 - Samples

Sample	Sampling site	Origin
A-124486	Air heater exit (9)	Smoky River
A-126286	Furnace wall (6)	Grande Caché
A-126486	End (8 and 10-14)	(Alberta)
A-126586	Electrostatic precipitator, cell a	MacIntyre Mine Ltd.
A-126686	Electrostatic precipitator, cell b	coking coal
A-126786	Electrostatic precipitator, cell c	
A-92488	End (8 and 10-14)	
A-92288	Furnace wall (6)	
Run 14-BC	Baghouse BC plant	Mt. Kaplan anthracite
Run 16-BC	Baghouse BC plant	Minto coal Havelock limestone
860114-Q	Baghouse Queen's Univ. plant	Mt. Kaplan coal (BC anthracite). Sand
850508	Baghouse Queen's Univ. plant	Devco coal Sysco limestone
S10-609#2D	Baghouse Chatham FBC unit Brunswick	Devco coal Havelock limestone

Samples A-See Fig.6; BC (British Columbia)-See Fig.7; Queen's-See Fig.8.

Table 2 - Analysis of samples

All figures are % by weight of samples.

Sample	C_{tot} (Coul)	C_{tot} (IR)	C_{in}	C_{org}	C_{el}	AI	LOI	Matrix
A-124486	7.44	7.36	0.07	6.72	0.65	7.52	8.24	coal
A-126286	14.5	14.6	0.02	13.0	1.43	14.46	18.54	"
A-126486	11.0	11.3	0.024	11.1	0.00	11.8	16.91	"
A-126586	9.06	8.95	<0.01	9.02	0.04	9.51	9.94	"
A-126686	5.18	5.36	<0.01	2.90	2.28	5.46	5.73	"
A-126786	3.13	3.22	0.01	1.55	1.57	3.56	3.71	"
A-92488	12.9	13.2	<0.01	12.72	0.18	13.62	14.76	"
A-92288	30.7	30.9	<0.01	30.26	0.44	30.39	34.39	"
Q-850508	5.34	5.47	0.06	5.37	0.00	4.37	18.15	coal + limestone
Q-860114	8.16	8.32	0.74	7.53	0.00	4.23	13.30	anthracite + sand
BC-Run 14	12.7	13.0	0.02	12.5	0.18	6.02	14.69	anthracite
BC-Run 16	3.43	3.44	0.44	2.62	0.37	2.40	4.69	Minto coal + limestone
S10-609#2D	7.86	7.84	0.58	5.74	1.54	6.77	11.54	Devco coal+ Havelock limestone

Table 3 - Analysis of spiked samples

All figures are % by weight of sample.

Sample	C_{tot} (Coul)	C_{tot} (IR)	C_{in}	C_{org}	C_{el}	AI	Matrix
126486-S	22.4	22.5	0.02	13.9	8.5	20.5	Residue
126486-C	9.8	10.2	0.02	9.7	0.2	10.3	of coal
D found	12.3	12.6	0.00	4.3	8.3	10.4	combustion
D real	12.2	12.2	0.00	6.05	6.1	---	(PSRB)
126586-S	20.5	19.8	0.01	11.2	9.4	18.2	Residue
126586-C	7.9	7.9	0.01	7.9	0.0	8.3	of coal
D found	12.6	11.9	0.00	3.3	9.4	10.6	combustion
D real	12.1	12.1	0.00	6.1	6.0	---	(PSRB)
850508-S	16.4	17.4	0.07	12.1	4.2	13.75	Residue of
850508-C	4.7	4.8	0.05	4.7	0.0	3.8	fluidized bed
D found	11.8	12.6	0.02	7.4	4.2	12.2	combustion of
D real	12.2	12.2	0.00	5.9	6.3	---	coal and limestone

Table 4 - Analysis of standards

All figures are % by weight of sample.

Data	Standard	C_{tot} (Coul)	C_{tot} (IR)	C_{in}	C_{org}	C_{el}	AI
Real	Standard 1	10.0		0.0	0.0	10.0	---
	Standard 2	9.87		0.0	9.87	0.0	---
	Standard 3	16.4		0.96	7.32	8.13	---
Analysis	Standard 1	10.6	10.8	<0.01	0.25	10.4	10.14
	Standard 2	9.6	9.6	<0.01	9.5	0.1	6.96
	Standard 3	16.6	16.7	0.93	7.73	7.94	14.96

Digestion Vessel Assembly

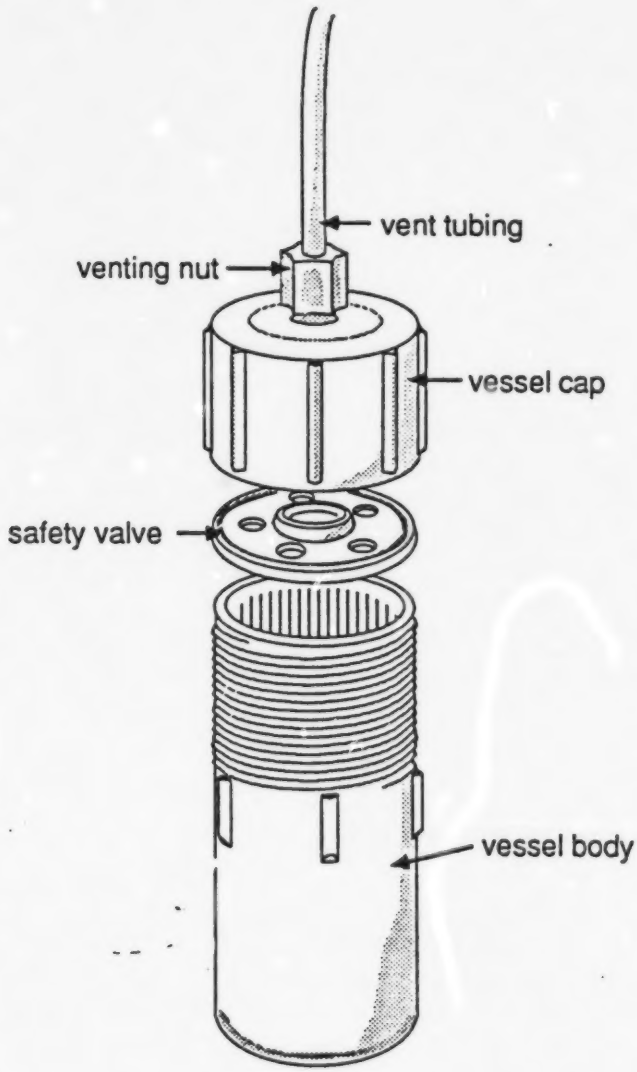
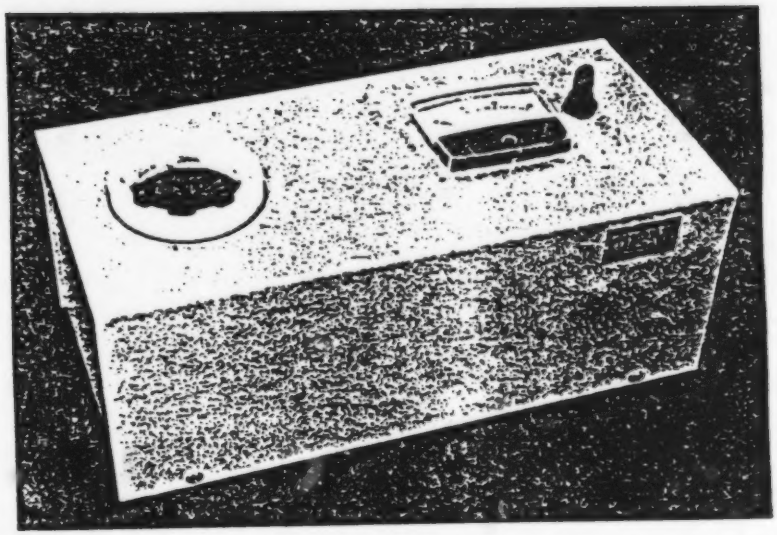


Figure 1 - Digestion vessel assembly

Capping Station



Capping Station Controls

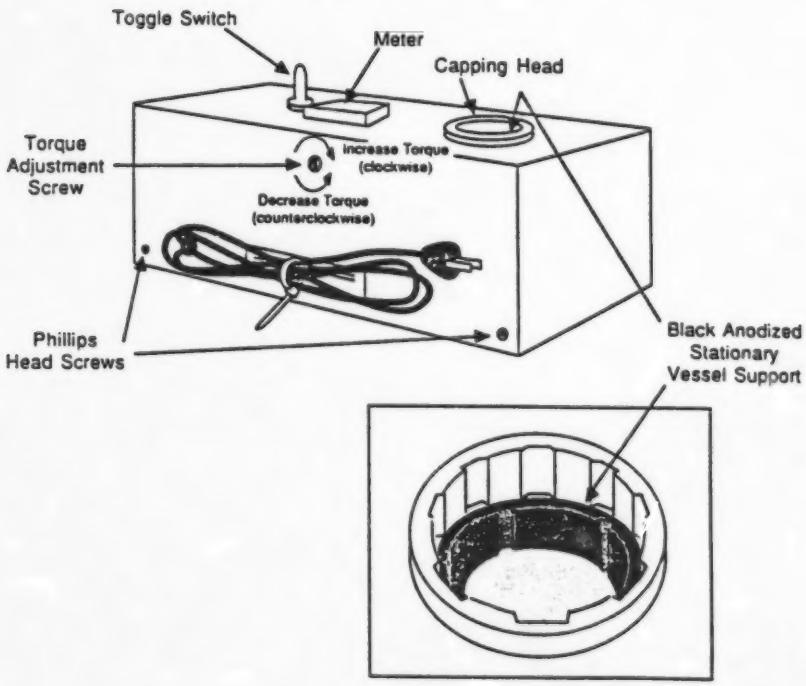
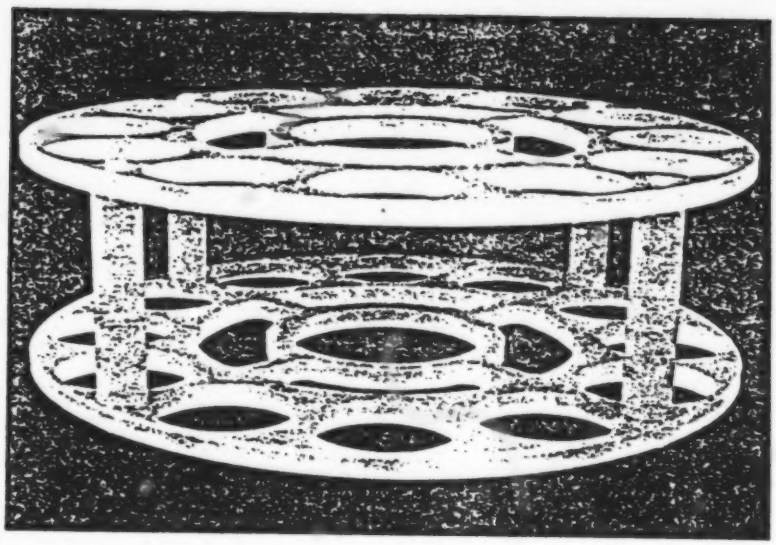


Figure 2 - Capping station and capping station controls

Turntable



Inserting a Venting Tube Into the Collection Vessel

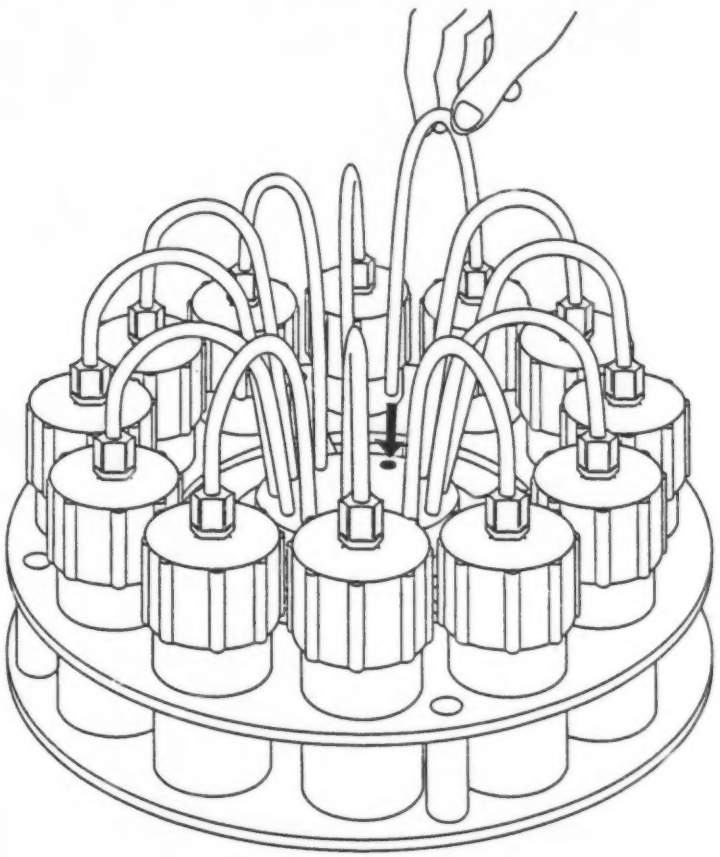
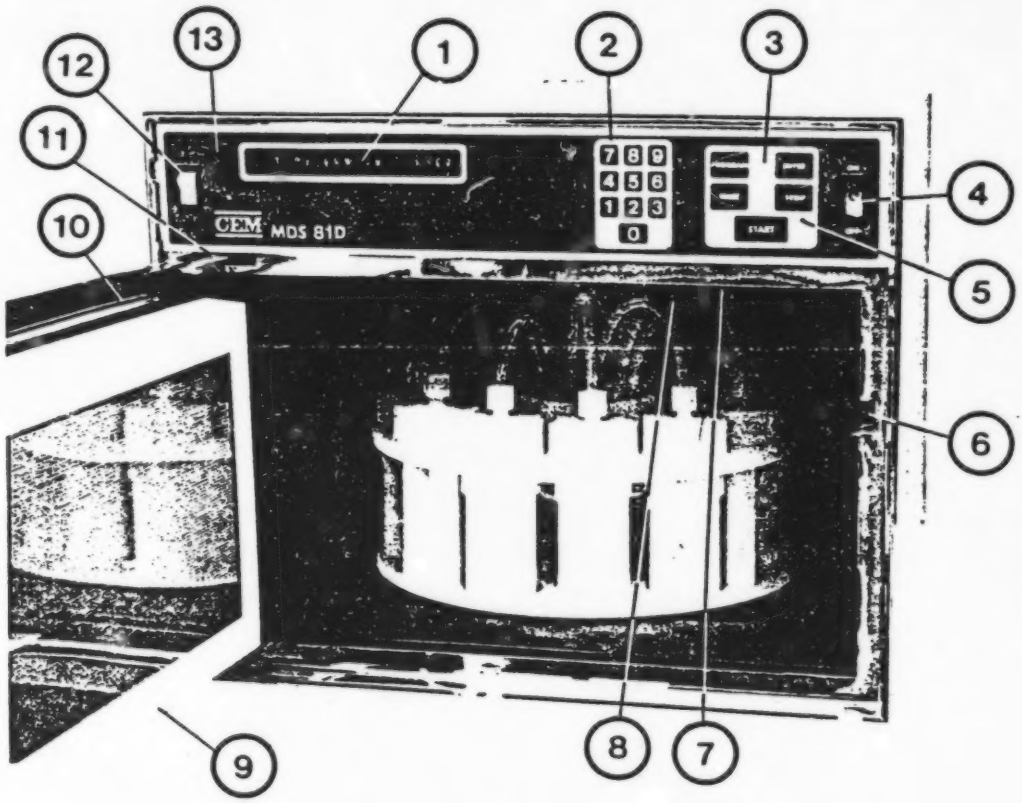


Figure 3 - Turntable



MDS-81D
Front View

1 20 Character Alphanumeric Readout
2 Control Setting Input Keys
3 Function Keys
4 Power Switch
5 Oven On LED Indicator
6 Door Safety Interlock
7 Mode Stirrer (Above False Ceiling)
8 False Ceiling (Remove For Closed Vessel Operation)
9 Door Inner Liner
10 Door Seal
11 Door Safety Interlock and Interlock Monitor
12 Turntable On/Off switch
13 Cavity Exhaust Blower Speed Control

Figure 4 - Digestion system - Front view

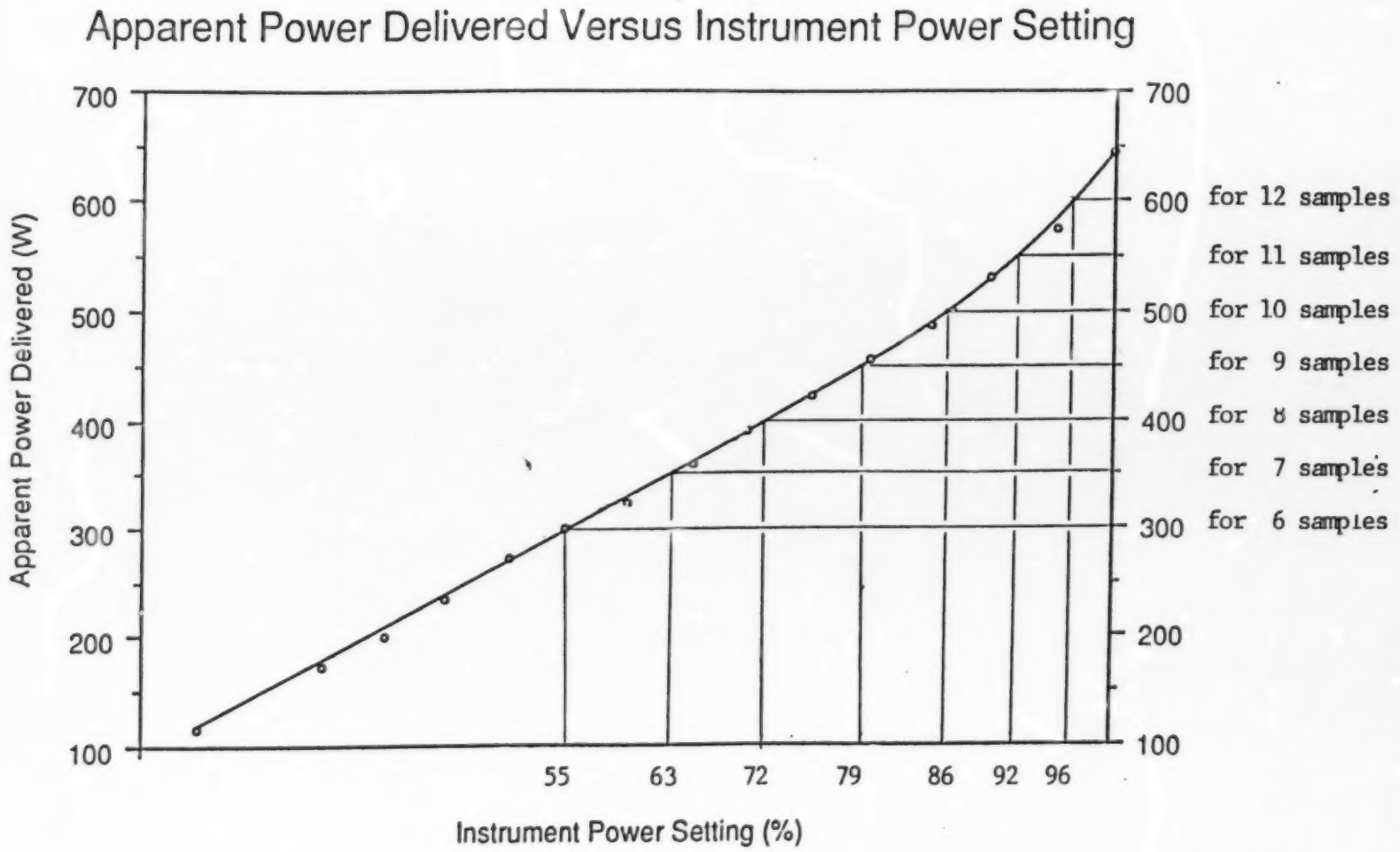


Figure 5 - Apparent power delivered as a function of power setting

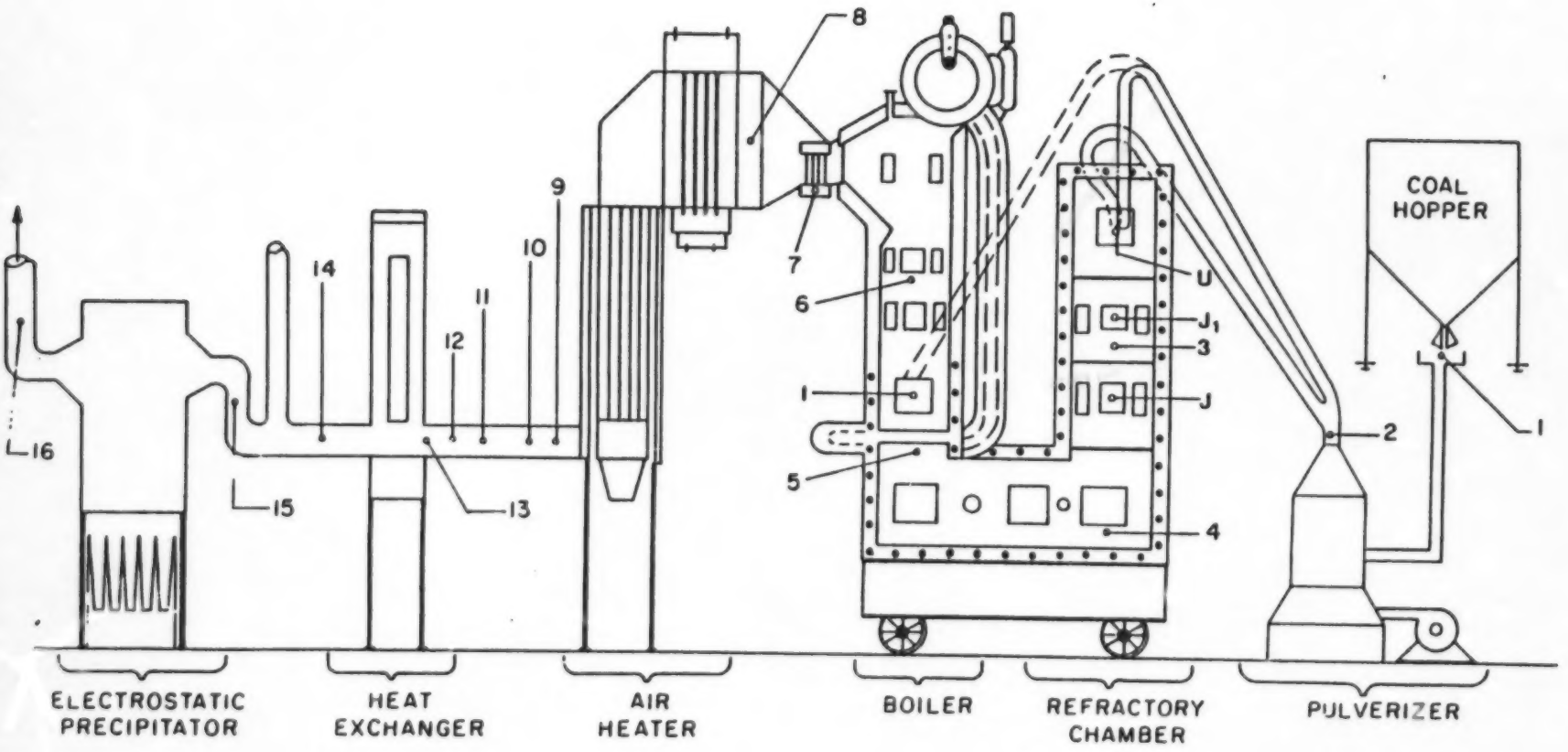


Figure 6 - Schematic diagram of Pilot-Scale Research Boiler (PSRB)

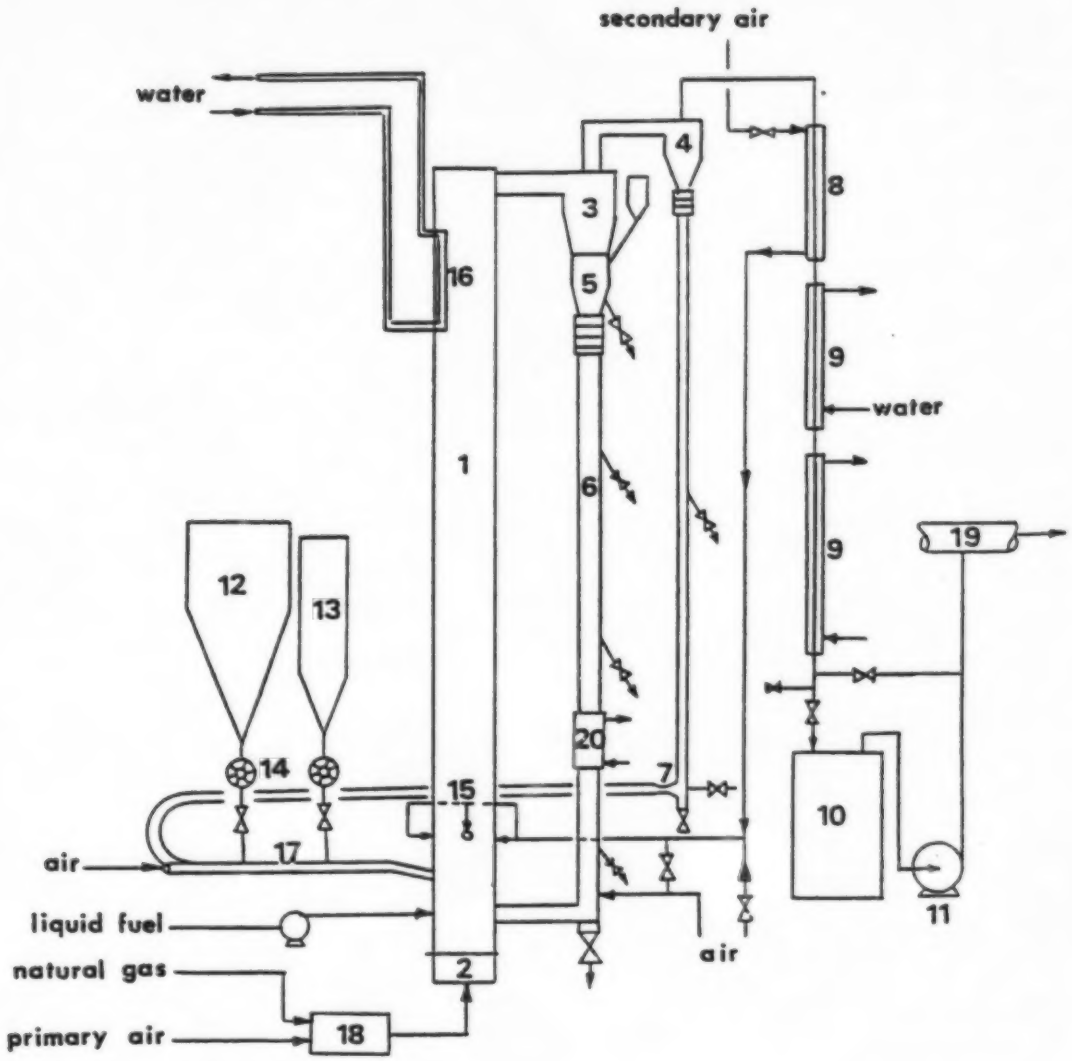


Figure 7: Simplified schematic diagram of circulating fluidized bed combustion facility (UBC).

1. Reactor; 2. Windox; 3. Primary cyclone; 4. Secondary cyclone; 5. Recycle hopper; 6. Standpipe; 7. Eductor; 8. Secondary air preheater; 9. Flue gas coolers; 10. Baghouse; 11. Induced draught fan; 12. Fuel hopper; 13. Sorbent hopper; 14. Rotary values; 15. Secondary air ports; 16. Membrane wall; 17. Pneumatic feed line; 18. External burner; 19. Ventilation; 20. Calorimetric section

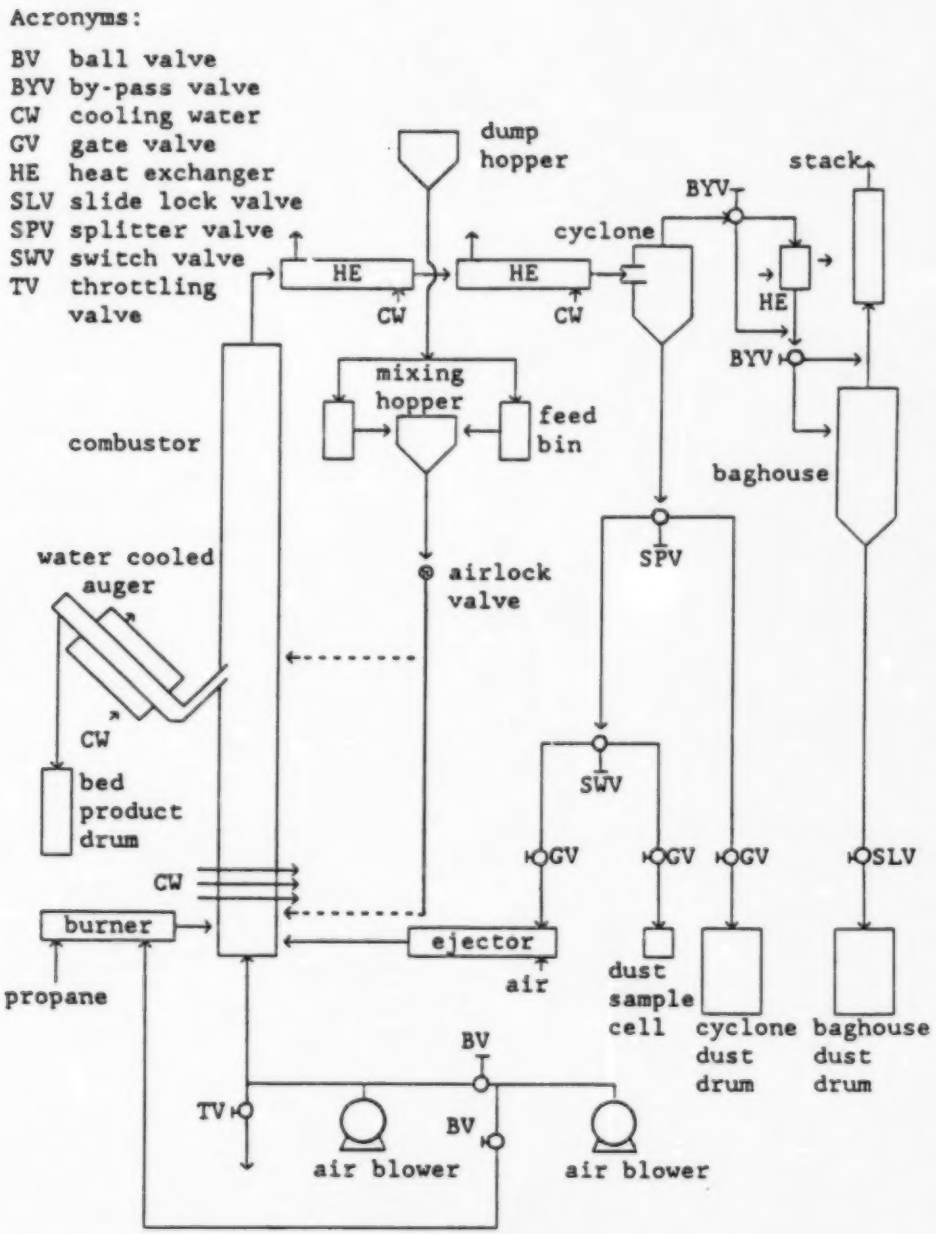


Fig. 8 - Flowsheet of AFBC pilot plant.